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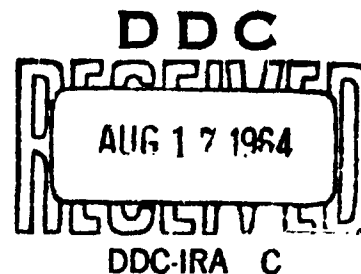
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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

ELEVENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 April - 30 June 1964

Contract No. NONR-3395(GG)
ARPA Order No. 23-65, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P



For

Director
Advanced Research Projects Agency
Washington, D. C.



MIDWEST RESEARCH INSTITUTE

M I D W E S T R E S E A R C H I N S T I T U T E

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by

Thomas A. Milne

Frank T. Greene

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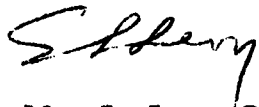
PREFACE

This report was prepared for the Advanced Research Projects Agency,
Washington, D. C.

The research staff consists of Dr. Thomas A. Milne, Project Leader,
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Approved for:

MIDWEST RESEARCH INSTITUTE



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10 August 1964

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SUMMARY

The aerodynamic molecular beam sampling system has been used successfully to sample stable products from several CO-O₂ flames. Oxygen free radicals have also been quantitatively sampled. Evidence is presented for a strong temperature dependence of the cracking patterns of the simple molecules HCl and CO₂.

I. INTRODUCTION

We have so far been attempting to determine, at least semi-quantitatively, the major effects encountered in mass spectrometric sampling of one atmosphere flames before going on to completely unknown metal systems.^{1/} During the last quarter we have concentrated on sampling stable product species and free radicals from flames using modulated beam techniques.^{2/} The following paragraphs describe some encouraging results in stable product sampling from flames as hot as 2800-2900°K, the quantitative detection of oxygen atoms in these flames, and an indirect determination of hydrogen atom concentration in rich $H_2-O_2-N_2$ flames. Evidence of significant variation with temperature of the cracking pattern of CO_2 and HCl is also given.

II. STABLE PRODUCTS AND OXYGEN ATOM CONCENTRATIONS IN $CO-O_2$ FLAMES

Four $CO-O_2$ flames, for which temperature and composition calculations were kindly supplied by Mr. Tom Dobbins, have proved very useful in testing our ability to quench species from very hot flames. These flames have initial ratios of CO/O_2 varying from 3:1 to 1:1 and burn easily on sheathed burners made from bundles of 20 gauge stainless steel tubing. Because of the low burning velocity of these flames and the nature of the reaction products, there is very little heating of the 0.005 in. thick water cooled sampling orifice. The tip of this spun, conical orifice is at a red-to-yellow heat with $CO-O_2$ flames under conditions where H_2-O_2 or CH_4-O_2 flames of the same temperature would "burn out" the orifice (presumably by melting) in a few seconds. Similar results are expected for $C_2N_2-O_2$ flames, which should be useful for temperatures above the 2800-3000°K obtainable with $CO-O_2$ flames.

The species CO , CO_2 , O_2 and O were measured for each of four $CO-O_2$ flames as a function of burner-to-orifice distance. It was established that at 20 ev (apparent electron energy as indicated on the Bendix electron energy grid - this was probably about 3 v. higher than actual electron energy) there were insignificant contributions to 16^+ from fragmentation of hot CO , CO_2 and O_2 , and therefore the 16^+ can be taken as a measure of O atom concentration. Similarly, the CO_2/CO ratios were determined at 25 ev where no significant fragmentation of CO_2 to 28^+ was observed.

Figure 1 (see page 6) shows typical profiles of these species through the burnt gas region of a 1:1 CO/O_2 flame. The more or less steady values at a distance of about 1 cm. are taken as the equilibrium values in the burnt gas

region. The marked rise in 16^+ as the orifice probe approached to within a few millimeters of the reaction zone is interpreted as showing that excess O atoms are generated in the primary reaction zone. It appears quite feasible to study quantitatively recombination processes such as $2O \rightarrow O_2$ in the burnt gas region of one atmosphere flames with improvements in the flame stability and uniformity, and perhaps with orifices smaller than the 0.005 in. diameter used in the current study in order to improve spatial resolution.

Table I shows a comparison of measured and calculated product concentrations for the four flames. The spectrometer was calibrated for sensitivity to CO_2 , CO, and O_2 by sampling known mixtures at one atmosphere and room temperature. In the case of O atoms the cross sections of O and O_2 were taken to be equal at 20 ev as indicated by the study of Fite and Brackmann.^{3/} A mass separation factor of 2 was also incorporated so that the deduced O/ O_2 ratio was a factor of 2 greater than the measured $16^+/32^+$ ratio. The results are in reasonable agreement with calculation. Actually, a complete analysis of these runs awaits direct measurement of the temperature in these flames. This will be attempted with our conventional sodium line reversal apparatus using a gas-filled tungsten strip lamp as a light source. Meanwhile, measured equilibrium constants (K_{eq}) for the $CO + (1/2)O_2 \rightarrow CO_2$ and the $O_2 \rightleftharpoons 2O$ equilibria, and their corresponding temperatures are compared with calculated values in Table II. As in our previous studies, it appears that equilibrium constants can be determined to within a factor of 2 - a criterion thought to be satisfactory for proceeding to unknown systems.

TABLE I

MEASURED AND CALCULATED PRODUCT PERCENTAGES IN CO- O_2 FLAMES

Flame (CO- O_2)	CO		O_2		CO_2		O	
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
1-1	15.1	(15.7)	38.7	(35.5)	46.1	(44.3)	2.5	(4.5)
4-3	20.8	(23.2)	28.7	(26.5)	50.6	(45.5)	2.4	(4.7)
2-1	30.9	(35.1)	13.8	(15.5)	55.4	(45.7)	1.6	(4.1)
3-1	48.3	(46.8)	4.82	(7.03)	46.9	(43.6)	1.0	(2.6)

TABLE II

MEASURED AND CALCULATED EQUILIBRIUM CONSTANTS FOR THE
REACTIONS $\text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2$ AND $\text{O} \rightleftharpoons 1/2 \text{O}_2$

<u>Flame</u> <u>(CO-O₂)</u>	<u>Meas.</u> <u>K_{eq.}</u>	<u>Temp.</u> <u>(°K)</u>	<u>Calc.</u> <u>K_{eq.}</u>	<u>Calc.</u> <u>Temp.</u>	<u>ΔT</u>
<u>$\text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2$</u>					
1-1	4.90	2874	(4.74)	(2885)	-11
4-3	4.54	2892	(3.80)	(2941)	-49
2-1	4.82	2875	(3.30)	(2977)	-102
3-1	4.42	2898	(3.65)	(2961)	-63
<u>$\text{O} \rightleftharpoons 1/2 \text{O}_2$</u>					
1-1	24.5	2733	(13.2)	(2885)	-152
4-3	22.0	2756	(10.9)	(2941)	-185
2-1	22.5	2752	(9.6)	(2977)	-225
3-1	20.9	2770	(10.1)	(2961)	-191

III. TEMPERATURE DEPENDENCE OF CRACKING PATTERNS OF SIMPLE MOLECULES

In the last quarterly report evidence was presented which indicated that fragmentation of CO_2 to CO^+ was appreciably greater at 1500-2500°K than at room temperature. Two experiments were performed to determine the magnitude of this change. CO_2 was added to a lean $\text{H}_2\text{-O}_2$ flame which burned at about 1950°K. There would be little CO in this lean flame at this temperature and the 28^+ observed at 50 ev could therefore be safely assigned to the fragmentation of hot CO_2 . Entrainment of N_2 was shown to be negligible. An approximately constant value of $44^+/28^+$ was obtained over the first 3 cm. beyond the reaction zone, indicating equilibration of the reaction $\text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2$. The results showed that the per cent of fragmentation of CO_2 to CO^+ varied from 11.5 per cent at room temperature to 17.3 per cent at 2000°K. This change is of the right order to explain some of the anomalous data for lean $\text{CH}_4\text{-O}_2$ flames previously reported.^{1/} A similar temperature effect was deduced from the $44^+/28^+$ ratios observed as 25 ev and 50 ev in the four CO-O_2 flames mentioned above. The CO_2 cracking pattern can be easily determined by always measuring CO_2/CO ratios at 25 ev, where fragmentation at any temperature of interest appears to be negligible.

Another test of the effect of temperature on fragmentation patterns was provided by studies of HCl in a series of rich $\text{H}_2\text{-O}_2\text{-N}_2$ flames which have been studied extensively by Sugden.^{4/} Profiles of 35^+ and 36^+ in the burnt gas regions of two such flames are shown in Fig. 2 together with the measured flame temperatures. Two things are of interest in these data. First, the limiting value of the $36^+/35^+$ ratio, well removed from the reaction zone, is smaller than for cold HCl and decreases as flame temperature increases. The HCl/Cl ratio is very large for even the hottest of the flames studied, and hence the $36^+/35^+$ represents the cracking pattern of HCl at these temperatures. The effect of temperature on the cracking pattern of HCl is comparable to that for CO_2 .

The second interesting feature of Fig. 2 is the marked drop in the $36^+/35^+$ ratio as the reaction zone is approached. Since the temperature is decreasing towards the reaction zone, this can only be interpreted as being due to significant Cl atom concentrations. The abrupt rise in the $36^+/35^+$ ratio at small distances occurs when the flame suddenly attaches to the cool sampling probe. Sugden^{4/} has argued that in such flames the reaction $\text{H} + \text{HCl} \rightleftharpoons \text{H}_2 + \text{Cl}$ will be much more quickly equilibrated than the recombination of H atoms. We can use our observed $36^+/35^+$ ratios, after correction for fragmentation, to deduce the HCl/Cl ratio as a function of distance in these flames. The concentration of H_2 in these rich flames is reasonably well known and can be measured

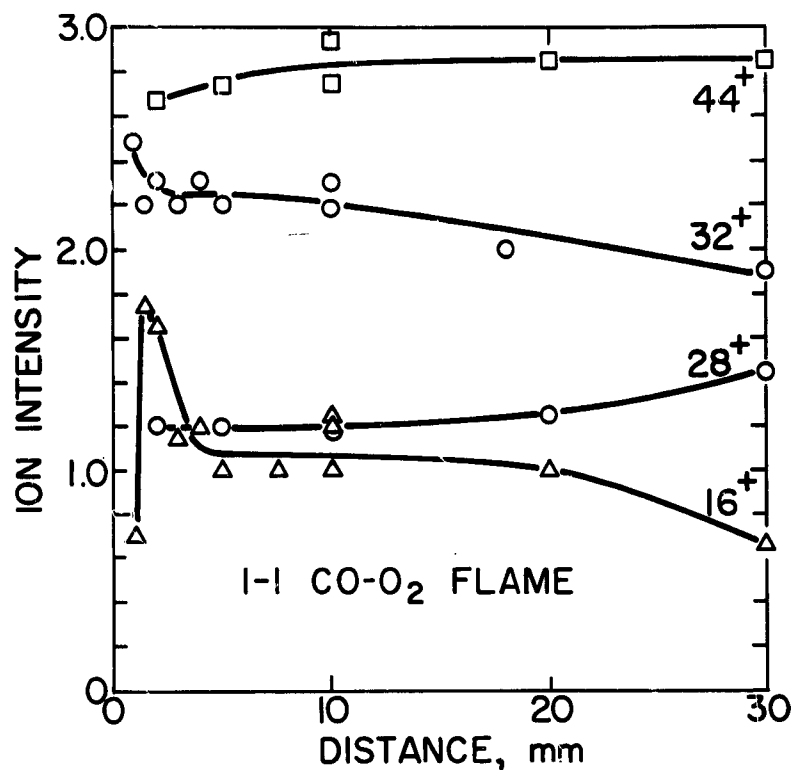


Fig. 1 - Product Concentration Profiles Downstream of the Reaction Zone of a 1:1 CO-O₂ Flame

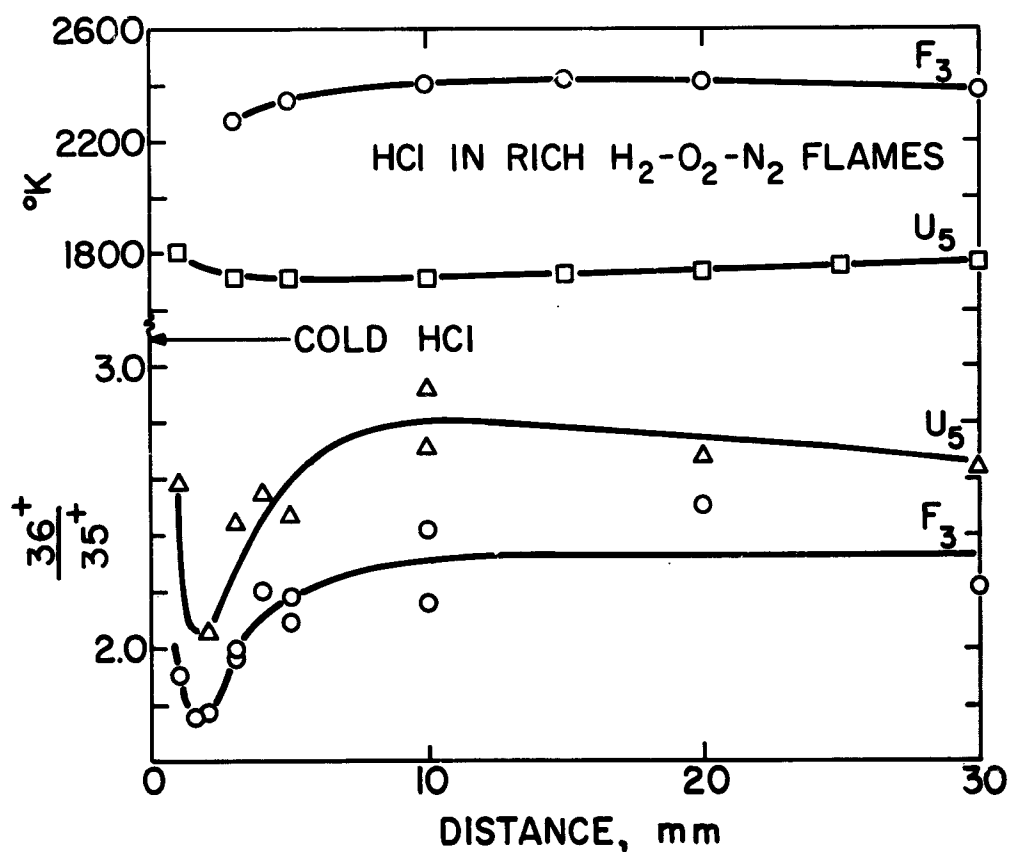


Fig. 2 - Temperature and 36⁺/35⁺ Profiles Downstream of the Reaction Zone of Two Rich H₂-O₂-N₂ Flames Containing HCl

directly. Hence, assuming equilibration of the above reaction, one can compute the H atom concentration in the flame near the reaction zone. From the data in Fig. 2 excess H atom concentrations as large as 400 and 5 times that at equilibrium are indicated for the flames U_5 and F_3 respectively. This method may prove valuable in later studies since it appears unlikely that H atoms can be directly measured with reasonable reliability due to the large mass separation effect.

In view of the large temperature effect on fragmentation of such simple molecules as CO_2 and HCl , it appears necessary to consider this effect in the study of a high temperature species where fragmentation may cause confusion. Likewise, caution should be used even in second law studies where parent ions are measured over considerable temperature ranges assuming constant ionization cross section.

IV. INSTRUMENTAL

As previously reported, the modulated beam system is now in routine operation. The beam is chopped at a nominal 10 cps by a vibrating reed, and the mass spectrometer output fed into a high-speed, low-noise relay which is phased with the beam chopper. The two signals thus obtained, which correspond to the shutter open and closed, are subtracted and integrated in an analog computer to obtain the net signal from the beam. Both analog outputs on the Bendix mass spectrometer have been incorporated into the modulated beam system, allowing two ions to be followed simultaneously.

Although the pulsed system has been generally satisfactory thus far, it is not yet clear whether the analog computer will be used in the final system. Some noise is certainly generated in the computer. Furthermore, the computer stability has not been carefully checked. It may therefore be necessary to use more sophisticated circuitry for very precise work. Further analysis of the present system, including the degree of discrimination of beam from background, will be carried out.

It is interesting to note that, although the manual shutter and modulated beam gave essentially identical results when stable gases were sampled, different results were obtained when an ion was produced from both stable and unstable species. This latter case arose when studying a flame containing both oxygen atoms and molecules. The manual shutter gave a smaller $16^+/32^+$ ratio than the pulsed beam because the manual "shutter dependence" for 32^+ included a component from the random gas introduced into the ion source by the scattered beam, and which was pumped out when the beam was interrupted. The scattered oxygen atoms, on the other hand, were destroyed by collision with the walls of the ion source.

One instrumental problem has arisen which may be worth reporting. Upon running ionization efficiency curves at relatively large trap currents, a curious, and very annoying, set of dips and wiggles was obtained. These were absent at lower trap currents. This effect is thus far unexplained.

V. FUTURE STUDIES

Attempts to quantitatively sample the OH radical will be made. Other known systems may be measured or repeated to round out the quantitative testing of the sampler. The major effort will be on adding metals to flames and on the sampling of condensible species. Oxides and hydroxides of the alkali and alkaline earth metals, the species H₂O, and the hydrated aluminum oxide species are of most immediate interest.

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